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(54) EMULSION POLYMERIZATION OF CHLOROPRENE

(71) We, TOYO SODA MANUFACTURING CO. LTD., a Japanese Company, of No. 4560, Oaza-sonda, Shin-Nanyo-shi, Yamaguchi-ken, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to aqueous emulsion polymerizations of chloroprene. More particularly, the invention relates to a process for producing a polychloroprene latex.

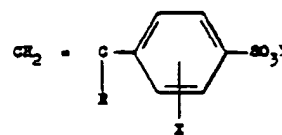
The term "polychloroprene latex" means an aqueous latex of a homopolymer or a copolymer of chloroprene.

In conventional alkaline aqueous emulsion polymerization reactions of chloroprene, it is usual to use an emulsifier, e.g. a metal salt of a resin acid, together with an auxiliary emulsifier, e.g. a condensate of formaldehyde and sodium naphthalenesulfonate. The auxiliary emulsifier is used for the stabilization of the latex when the latex is made acidic when the polymer components are separated from the latex e.g. by freeze coagulation. However, the auxiliary emulsifier is only physically adsorbed onto the surface of the particles of the latex, and therefore the emulsifier may pass into the washing water when the polymer is washed. As a result, the chemical oxygen demand of the washing water is increased. However, when only a metal salt of a resin acid is used as the emulsifier, the latex is unstable and tends to precipitate the polymer when the pH of the latex becomes acidic. It is possible to precipitate the polymer components for example by a freeze coagulation when the latex is alkaline, but even in the latter case, the emulsifier is physically adsorbed onto the surface of the particles of the latex, and therefore may contaminate the washing water and increase the chemical oxygen demand. The same phenomenon is observed for acidic emulsion polymerization using an acidic emulsifier.

The inventors of the present invention have

attempted to overcome these disadvantages and have found that a polychloroprene latex can be produced by using at least one anionic or nonionic emulsifier and a particular ethylenically unsaturated aromatic sulfonic acid or salt thereof.

According to the invention there is provided a process for producing a polychloroprene latex which comprises polymerizing chloroprene or a mixture of chloroprene and a comonomer in the presence of at least one anionic or nonionic emulsifier and an ethylenically unsaturated aromatic sulfonic acid or a salt thereof having the formula



wherein R represents a hydrogen atom or a C_1 — C_4 alkyl group; X represents, H, C_1 — C_4 alkyl group, a halogen atom, or a hydroxyl group; and Y represents a hydrogen atom, a potassium or sodium atom or a quaternary ammonium group.

It is an advantage of the present invention, at least in preferred embodiments, that it can provide a latex containing an emulsifier which can be used to produce a solid polymer from which the emulsifier is not leached by washing water because the emulsifier is chemically bonded to the particles of the latex instead of being held merely by physical forces as in conventional latices.

Typical comonomers having ethylenically unsaturated double bonds and which are copolymerizable with chloroprene and which can be used in the present invention include conjugated dienes e.g. 1 - chlorobutadiene, 2,3 - dichlorobutadiene, 2 - cyanobutadiene, butadiene and isoprene and other comonomers e.g. styrene, acrylonitrile, acrylates and methacrylates. Preferably the amount of the comonomer is 50 wt. % or less of the total monomers.

The emulsifiers used in the present invention can be conventional anionic or nonionic

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emulsifiers e.g. metal salts of resin acids, metal salts of fatty acids, alcohol sulfates and polyoxyethylene alkyl ether sulfates. The emulsifier is usually added in an amount corresponding to 0.1—10 wt. % and preferably 0.5—5 wt. % of the total monomers, including the aromatic sulfonic acid or salt thereof.

Typical ethylenically unsaturated aromatic sulfonic acids and salts thereof which can be used in the present invention include p-styrenesulfonic acid, α -methylstyrenesulfonic acid, o-chlorostyrenesulfonic acid and o-methylstyrenesulfonic acid and potassium, sodium or quaternary ammonium salts thereof. The compound is usually added to the reaction mixture in an amount corresponding to 0.1—10 wt. % and preferably 0.5—5 wt. % of the total monomers, including the aromatic sulfonic acid or salt thereof.

Molecular weight regulators are usually used in the polymerization reaction and can be the conventional ones used for emulsion polymerization. Typical molecular weight regulators include alkyl mercaptans, alkyl-xanthogendisulfides and halogenated hydrocarbons. Radical initiators are also usually used in the polymerization reaction and these can also be conventional ones, e.g. potassium persulfate and alkylhydroperoxides.

The emulsion polymerization of the invention is usually carried out at 0—100°C and preferably at 10—60°C. The polymerization reaction is terminated by adding a conventional terminating agent when the conversion reaches a predetermined limit. Any unreacted monomer can be removed, for example, by a vacuum treatment at high temperature.

A further understanding of the invention can be obtained by reference to the following References and Examples. In the Examples, the term "parts" means part by weight unless otherwise specified.

In the References and Examples 10 g of the latex produced is taken as a sample and placed on a stainless steel dish having an area of 48 cm², and the latex is then coagulated by freezing. The resulting coagulated polymer is immersed in 100 g of water for 40 hours. The chemical oxygen demand (COD) of the water after the immersion is then measured and the results are given in each case. It is found that the CODs of latex polymers produced by the invention fall in the range of 100—500 ppm, which is remarkably low compared with a COD of 3000—6000 ppm when only conventional emulsifiers are used.

Reference 1

A polymerization reaction was conducted as follows in a 5 litre stainless steel reactor equipped with a stirrer and a heating jacket. 100 parts of water, 2.0 parts of disproportionated rosin soap as an emulsifier and 2.0 parts of formaldehyde-sodium naphthalene-

sulfonate condensate were charged to the reactor under a nitrogen gas flow. 100 parts of chloroprene containing 0.3 part of n-dodecyl mercaptan was added to the mixture with stirring. When the temperature of the mixture reached 40°C, 0.01 part of potassium persulfate was added to initiate the polymerization. When the conversion reached 60%, para - t - butyl catechol was added to the reaction mixture to terminate the polymerization.

After adding the terminating agent, the unreacted monomer was recovered from the resulting latex by a flash-distillation under reduced pressure. 10 g of the latex was placed as a sample on a stainless steel dish having an area of 48 cm² and was coagulated by freezing to produce a polymer sheet. The sheet was immersed in 100 g of water for 40 hours to simulate washing. The chemical oxygen demand (COD) of the resulting water was 5100 ppm.

Reference 2

The process of Reference 1 was repeated except that 4.0 parts of sodium laurylsulfate was used as the emulsifier. The chemical oxygen demand of the washing water was 6000 ppm.

Example 1

100 parts of water, 2.0 parts of disproportionated rosin soap and 2.0 parts of sodium p-styrenesulfonate as the emulsifiers were charged to the reactor described in Reference 1 under a nitrogen gas flow. 100 parts of chloroprene containing 0.3 parts of n-dodecyl mercaptan was added to the mixture with stirring. The polymerization was conducted in accordance with the process described in Reference 1. The chemical oxygen demand of the washing water was 230 ppm.

Example 2

The process of Example 1 was repeated except for the use of 2.0 parts of sodium laurylsulfate and 2.0 parts of p-styrenesulfonic acid as the emulsifiers and also the use of a mixture of 90 parts of chloroprene and 10 parts of 2,3-dichlorobutadiene instead of the 100 parts of chloroprene. The chemical oxygen demand of the washing water was 370 ppm.

Example 3

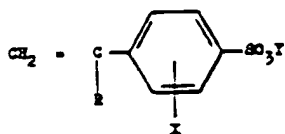
The process of Example 1 was repeated except for the use of 0.5 part of sodium laurylsulfate and 3.5 parts of sodium o-chlorostyrenesulfonate as the emulsifiers, and the use of a mixture of 90 parts of chloroprene and 10 parts of styrene instead of the 100 parts of chloroprene. The chemical oxygen demand of the washing water was 180 ppm.

Example 4

The process of Example 1 was repeated except for the use of 2.0 parts of polyoxy-ethylenealkyl ether sulfate and 2.0 parts of ammonium o-methylstyrenesulfonate as the emulsifiers. The chemical oxygen demand of the washing water was 430 ppm.

WHAT WE CLAIM IS:—

1. A process for producing a polychloroprene latex which comprises polymerizing chloroprene or a mixture of chloroprene and a comonomer in the presence of at least one anionic or nonionic emulsifier and an ethylenically unsaturated aromatic sulfonic acid or a salt thereof having the formula



wherein R represents a hydrogen atom or a C_1-C_4 alkyl group; X represents a hydrogen atom, a C_1-C_4 alkyl group, a halogen atom, or a hydroxyl group; and Y represents a hydrogen atom, a potassium or sodium atom or a quaternary ammonium group.

2. A process according to claim 1, wherein the chloroprene content in the mixture of chloroprene and the comonomer is 50 wt. % or more.

3. A process according to claim 1 or claim 2 wherein the ethylenically unsaturated aromatic sulfonic acid or salt thereof is selected from p-styrenesulfonic acid, α -methylstyrenesulfonic acid, o-chlorostyrenesulfonic acid, o-methylstyrenesulfonic acid and potassium, sodium and quaternary ammonium salts of the said sulfonic acids.

4. A process according to any preceding

claim wherein the polymerization mixture contains 0.1—10 wt. % of the anionic or nonionic emulsifier, based on the total weight of the monomers, including the aromatic sulfonic acid or salt thereof.

5. A process according to any preceding claim wherein the polymerization mixture contains 0.1—10 wt. %, of the ethylenically unsaturated aromatic sulfonic acid or salt thereof, based on the total weight of the monomers including said aromatic sulfonic acid or salt thereof.

6. A process according to any preceding claim wherein the comonomer is selected from conjugated dienes, styrene, acrylonitrile, acrylates and methacrylates.

7. A process according to any preceding claim wherein the anionic or nonionic emulsifier is selected from metal salts of resin acids, metal salts of fatty acids, alcohol sulfates and polyoxyethylene alkylether sulfates.

8. A process according to any preceding claim wherein the polymerization is carried out at a temperature of 0—100°C.

9. A process according to claim 8 wherein the polymerization is carried out at a temperature of 10—60°C.

10. A process for producing a polychloroprene latex substantially as described herein with reference to any one of the Examples.

11. A polychloroprene latex produced by a process according to any preceding claim.

12. A solid polymer obtained from a latex according to claim 11.

R. G. C. JENKINS & CO.,
Chartered Patent Agents,
Chancery House,
53/64 Chancery Lane,
London, WC2A 1QU.
Agents for the Applicants.

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